Advanced Transition Metal Chemistry – Metal-Metal Bonding

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Lecture – 25

Preparation of Important and Useful Metal Complexes

Hello everyone. Once again, I welcome you all to MSB lecture series on transition metal chemistry. This is 25th lecture in the series. In this lecture, I shall give you the preparation of important and useful metal complexes keeping the catalysis and also further interesting organometallic compounds in mind. So, let me begin with some compounds of palladium.

So, for example if we just look into palladium metals such as ruthenium, palladium, platinum, gold, rhodium, iridium, these compounds are quite extensively used in homogeneous catalysis for a variety of organic transformations. Then how to make some of these compounds and what are the properties of these compounds that can be used as precursors for further substitution and making desired compounds with desired ligands to guide the reactions in the name of homogeneous catalysis.

So, you cannot use any complex that comes to your mind for catalysis, well-defined ligands should be there and well-defined metals should be there and also precise oxidation state has to be chosen and such complex has to be chosen and what kind of coordination numbers should be there to begin with. If one or two ligands leave or dissociate, what kind of compound we are going to get? Whether that can be a catalytic precursor or not?

So, when we keep all those things in mind, we come up with an excellent ligand system, then we need an appropriate metal precursor for further substitution reaction to make the desired compound. simply you cannot use any compound. From that point of view, I shall give you the preparation of very important compounds.

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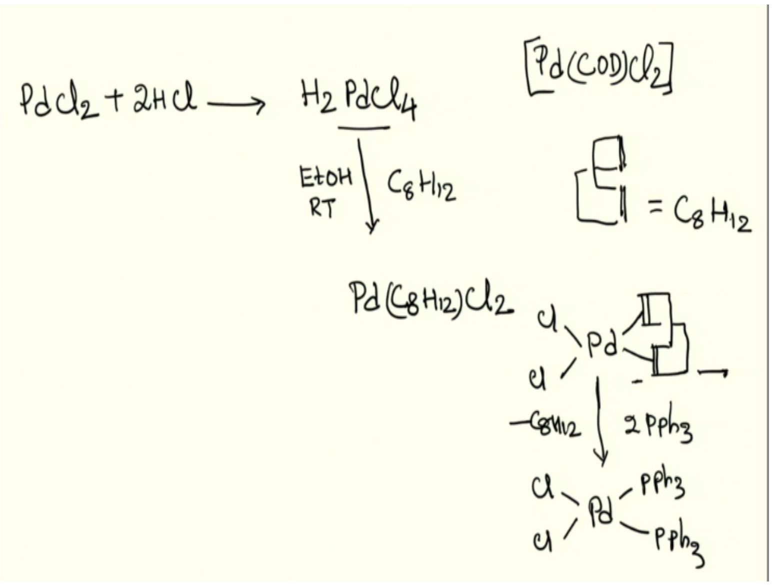

Let me begin with palladium(cod)chloride. You must have heard about Pd(COD)Cl_2. So, cod is cyclooctadiene, it is very easy to write. It is a diene, a bidentate ligand. So, this is cod, cyclooctadiene. Then how to make this compound? The starting compound is palladium chloride. You take palladium chloride and palladium chloride if you take as such is insoluble in organic solvents and also is insoluble in water.

As a result, what you should do is you add HCl. Once you add HCl it forms palladic acid something like this and this is soluble now. This is the first step. Take anhydrous palladium chloride, add HCl and then generate this species here. Once generating this species, treat this one with C_8H_{12}. So, this is C_8H_{12}. Of course, this reaction does not need any heating or anything. This reaction can be carried out at room temperature in ethanol.

So, you should remember in future if I write RT, means it is room temperature. What we get is, if you are curious to know the structure, this is how the structure looks like. This is Pd(COD)Cl_2. This is very useful. For example, you take this compound, let us say treat with two equivalents of triphenylphosphine in dichloromethane, these two triphenylphosphine molecules would replace this bidentate ligand, then we get a compound like this.

So, this cyclooctadiene being a diene has a characteristic smell and this compound does not have any smell, but the moment you treat with two equivalents of triphenylphosphine then this cod is liberated. When the cod is liberated, you can see the smell coming, characteristic smell of olefine comes out, so that indicates that reaction is progressing and also there can be colour change. This is a bright yellow colour and this will be slightly yellow or even pale yellow in colour.

So visually you can monitor and also if you are careful, through smell you can make out that reaction is progressing. Of course, once this compound is made, you can crystallize and take NMR and NMR should show a single phosphorus resonance indicating this one, and in case if there are two isomers, then you should be able to see two ^{31}P chemical shifts indicating cis and trans isomers.

So, with this reaction usually you get a cis isomer. So, this is the utility. Not only this one, if you want to use any other ligands, bidentate ligands you should be able to use conveniently starting from Pd(COD)Cl_2.

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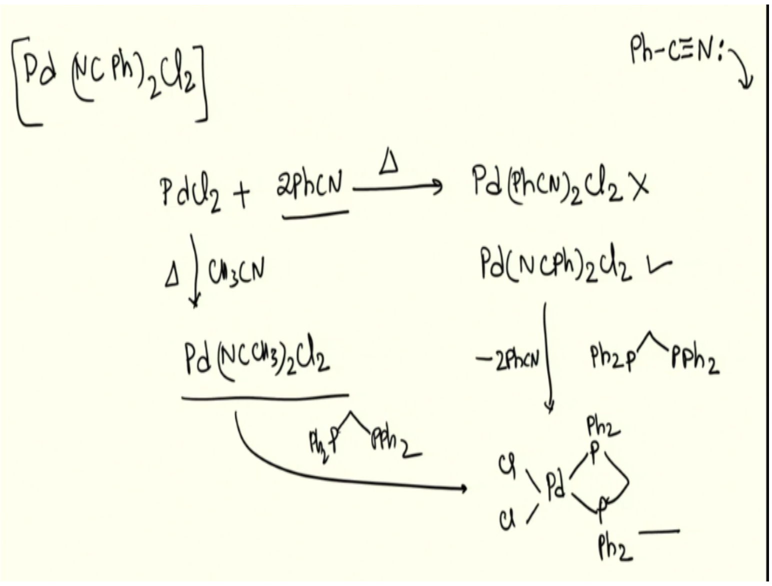

So, another important compound is bis benzonitrile compound. So, here this is very similar to the previous one, instead of cyclooctadiene, we are using PhCN ligand here. This is a nitrile, so this lone pair is there. This lone pair goes to the metal, that means, this forms a very weakly coordinated compound, but moderately stable bright yellow powder, we can handle even in atmosphere without any problem.

So, how to prepare this compound? Take this palladium chloride here and add excess and reflux you get this compound here. Of course, one can also write like this fashion, but it is always appropriate to write ligand in such a way that that donor atom is facing the metal centre, this is not correct, one should write something like this. This is also very useful compound. In this case also, you take again a bidentate ligand, consider for example a bidentate ligand such as this one. This is called bis(diphenylphosphino)methane.

It is a methyl derivative, and a bidentate ligand. You take this one and two benzonitriles will come out and you get a compound like this, a chelate compound. So, this is how one can make some of these very labile metal precursors and conveniently without losing this compound or further decomposition, you can get quantitative yield of compounds depending upon what kind of ligands you are using.

And if benzonitrile is not available, it should not be a problem. You take this palladium chloride and take dry acetonitrile, freshly distilled acetonitrile or methyl cyanide in excess reflux it for about 2 to 3 hours, you will see the formation of bright yellow coloured solution that is due to be bis(acetonitrile) complex formation. This compound is unstable compared to benzonitrile analog.

As a result, whenever we need this can be generated in situ and without isolating one can use it. If you want to isolate this one, as bright yellow crystals, it has to be stored under nitrogen in airtight bottles. So, this is another important precursor and sometimes what happens there is no need to isolate this one. Take palladium chloride and reflux in dry acetonitrile for 2 hours and then add ligands, whatever the ligands you want to add.

Add and substitution would be complete and you can quantitatively convert bis acetonitrile compound into corresponding compound. For example, you take here add, you can get this compound, so like this. So, these three are very important compounds and very easy to make, commercially if you try to buy they are very expensive, but on the other hand palladium chloride is little cheaper and one can conveniently make these compounds and also even yields are quantitative.

So, you start with palladium chloride and since we are increasing its molecular weight by two-fold, you can see, start with 1 gram you can get 3 to 4 grams. So, that is the advantage of learning these preparatory methods to prepare in your own laboratory, instead of buying all those things commercially.

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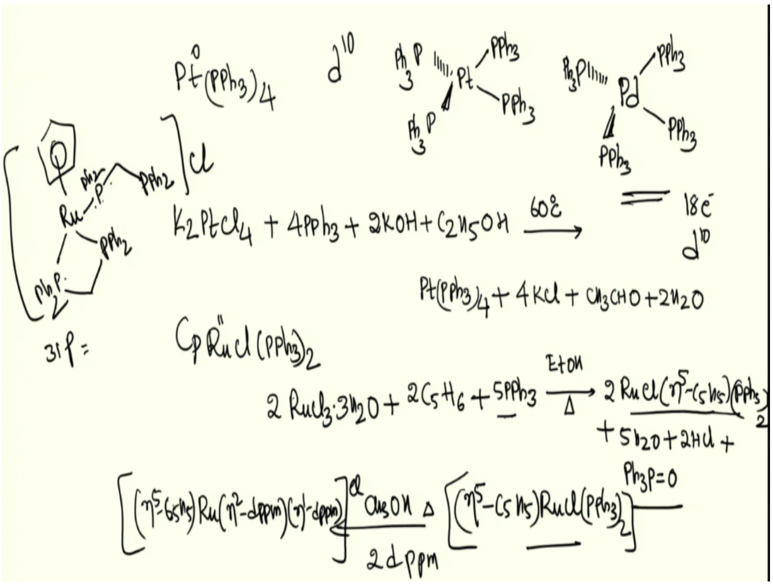

Next, consider one more compound. This is tetrakis(triphenylphosphine)platinum compound This is one of the very useful platinum zero compound here, a d^{10} system and d^{10} system is you should remember that it has tetrahedral geometry. Similarly, one can also make palladium compound. This is most useful palladium zero compound. This is an 18 electron species, d^{10}, for homogeneous catalysis and it is commercially available.

Many reactions, carbon-carbon cross coupling reactions or hydrogenation and for many other reactions, people use this one and this compound; can be made again easily. So, let us look into first platinum compound preparation. For this one we are using potassium tetrachloroplatinate that is K_2PtCl_4. Take this one, add 4 equivalents of triphenylphosphine in presence of alcoholic KOH that is for reduction purpose and this has to be heated to 60 °C. Remember temperature is very critical.

It should not go beyond 60, 60 to 62 °C. If it goes beyond what happens, the yield will reduce. So, take a mixture of potassium tetrachloroplatinate, 4 equivalents of triphenylphosphine in presence of alcoholic KOH what you get is, what are the other byproducts, I am writing them also. So, this is the balanced equation for the preparation of $Pt(PPh_3)_4$ starting from potassium tetrachloroplatinate.

Another important compound of platinum metals is ruthenium complexes. Ruthenium is in +2 state here because two anionic ligands are there, one is Cp, one is chloride. Then how to make this compound? For most of these compounds we use trichloride trihydrate, you should remember in case of iridium, ruthenium and rhodium we are using +3 compounds $MCl_3.3H_2O$ they are ideal ones.

And in case if they have nH_2O, using an appropriate method, you have to generate first anhydrous salts and then you make the trihydride compound. These trihydride compounds are quite reactive and convenient to prepare a series of interesting organometallic compounds and also coordination compounds which can be further used in various applications. One such important application is again homogeneous catalysis.

For this one, for the preparation of this Ru^{II} complex having 2 triphenylphosphine and one cyclopentadienyl group and one chloride one has to start with ruthenium trichloride trihydrate and take two equivalents of cyclopentadiene. So, this should be freshly distilled. So, for example if you take cyclopentadiene and if you keep it at room temperature for a prolonged time, so it undergoes dimerization to form cyclopentadienyl dimer.

So, this dimer has to be cracked into monomer, simply by distilling it you can convert into monomer, immediately you have to use it, that means you have to generate quickly, you have to distil quickly and then you have to use it. Otherwise, what happens you will end up with a dimer and that does not react with this metal precursor. So, take this one and treat this with 5 equivalents of triphenylphosphine.

So, take ethanol and reflux it, so you get this one, along with this, you also get. For this purpose, what we are doing is we are using excess of one equivalent of triphenylphosphine that leads to the formation of phosphineoxide and this acts as a reducing agent here. And one thing you should remember, one can write something like this, there is no harm, but to be precise when we have these automatic groups with the different hapticity, it is always ideal to write that ligand in the front.

So, best way to write is in this fashion, this is a correct way of writing. So, this also useful compound. For example, in this one, one can also replace two equivalents of triphenylphosphine with a bidentate ligand, because the entropically that is a favoured one with chelate ligand. So, you can replace this one or if you are using excess, what happens you can use a polar solvent, so that you can ionize Ru—Cl bond and it becomes cationic compound.

So, if you use nonpolar solvents, you can simply substitute triphenylphosphine with desired ligands, bidentate ligands or monodentate ligands which are better sigma donors compared to triphenylphosphine or if you want to use slightly excess to even get rid of chloride you have to go for a polar solvent. For example, take this compound and add 2 equivalents of bidentate ligands, let us say I am adding 2 equivalents dppm.

Dppm is bis(diphenylphosphino)methane I used in previous palladium complex. So, use this one in methanol and if you reflux it, basically what happens? It becomes ionic complex and then you have η^2 dppm and η^1 dppm and then you have chloride here. So, something like this happens. How this molecule looks like? You can see here, in this one, two ligands are there and a chloride is here, it becomes an ionic complex, so one can make it.

And how to know that this has two ligands, one is say monodentate ligand, one is bidentate ligand? ^{31}P NMR would tell you again. If you look into ^{31}P NMR spectrum of this complex 3 signals it would show. For example, these two are chelated, so they will be coupling with this one to show a triplet and then this would be coupling with this one as well as this one depending upon which one is larger, either it can be a triplet of doublets or doublet of triplets.

And then this is very far from this one, it may not couple with this one; simply it can show a doublet. And assignment and interpretation will be very easy and one can easily know simply by recording ^{31}P NMR spectrum, whether you made your compound or something else has formed. Of course, once these lectures are over and most of the aspects that I want to discuss are completed, I shall give you some hints about ^{31}P NMR and how to understand interpretation of data using various multinuclear NMRs.

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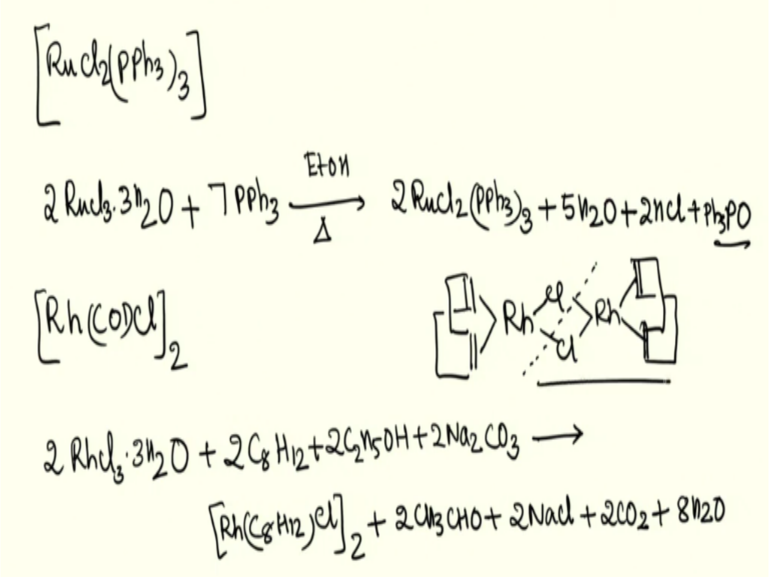

$[RuCl_2(PPh_3)_3]$

$$2\,RuCl_3\cdot 3H_2O + 7\,PPh_3 \xrightarrow[\Delta]{EtOH} 2\,RuCl_2(PPh_3)_3 + 5H_2O + 2HCl + \underline{Ph_3PO}$$

$[Rh(COD)Cl]_2$

$$2\,RhCl_3\cdot 3H_2O + 2\,C_8H_{12} + 2\,C_2H_5OH + 2\,Na_2CO_3 \longrightarrow [Rh(C_8H_{12})Cl]_2 + 2\,CH_3CHO + 2\,NaCl + 2\,CO_2 + 8H_2O$$

So now let me give the preparation of another interesting compound of ruthenium. This is also a very useful compound. How to prepare this one, in the same way as I described for the previous one starting with $RuCl_3.3H_2O$. Here simply we are taking excess of triphenylphosphine and refluxing this mixture in ethanol that leads to the formation of a ruthenium(II) compound plus.

So, here the role of excess of triphenylphosphine we are using is to act as a reducing agent. So, now let me tell you about a couple of rhodium complexes, rhodium(I) complexes, to make Wilkinson compounds, similar to Wilkinson compounds or other bisphosphine bound complexes of rhodium(I). So, these two precursors I am going to write are very important. The first one is rhodium cod dimer.

If you are curious to know the structure of this one, this is how it looks like. This is rhodium chlorocarbonyl dimer and of course if you can see here, when we do reactions, it symmetrically cleaves in this fashion to generate immediately a coordination site and then that coordinate site can be occupied by appropriate ligands. And if you further force the reaction using drastic conditions, you can also eliminate cod here and in this place another two ligands can come into the picture.

So that means it is quite versatile, either it can retain chloro bridges and substitute for cod or it can also break symmetrically to generate a vacant coordinated site on each rhodium and also it can be substituted. So, two options are there while using this one. So how to make this compound? Here again we are taking rhodium trichloride trihydride and then we are using cyclooctadiene and then we are using ethanol as a solvent and also as a reagent and we are using sodium carbonate a base.

This is the dimer, already I have written the structure here. So, this is how you can make this rhodium chlorocyclooctadiene dimer, very useful compound this one. And also from this one, one can also generate chlorocarbonyl dimer also or one can also use another method of directly reacting rhodium trichloride trihydride with carbon monoxide, very interesting reaction you can perform solid state reaction.

I shall tell you details about the preparation of that one and also how to further react this to get some important derivatives in my next lecture. Until that have an excellent time reading chemistry.